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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to the Preservation of Fruit

We, STANDARD FRUIT AND STEAMSHIP COMPANY, Inc., a corporation organized under the laws of the State of Delaware, United States of America, of 944 St. Charles Avenue, New Orleans, Louisiana, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method for preserving bananas and other fruits which ripen after being picked and wherein the ripening is accompanied by a breathing action. It is especially useful on bananas, and particularly to the crowns or stems of cut bananas, to prevent or retard their unsightly decay.

In its specific and preferred form, the invention consists in an application to the crowns or other cut surface of the fruit of a low melting point acylated glyceride, preferably in combination with an application of a fungicide or fungistatic agent.

As will appear from the following description, the invention finds a special application to bananas partly because of the nature of the fruit and partly because of the manner in which bananas must be handled from the time they leave the plant in the tropics to their points of use in other countries. When it is realized that the invention comprises a coating applied to the fruit, the pertinence of certain characteristics of the life cycle of the fruit will be appreciated.

According to some authorities (see such as J. B. Biale of the University of California, College of Agriculture, in Annual Review of Plant Physiology, 1950, page 183, *et seq.*) the life history of a fruit may be divided into five distinguishable stages namely; cell division, cell enlargement, maturation, climacteric, and senescence. The climacteric marks a transition phase between development and the onset of functional breakdown between ontogeny and senescence. The ontogenous climacteric is the marked and sudden rise in respiration of the fruit prior to senescence which takes place without the influence of external agents, although an induced climacteric may be brought about by the use of externally applied agents such as ethylene. This respiration must not be obstructed.

Referring particularly to bananas, the transition from green to yellow takes place during or immediately following the climacteric. The eating ripeness stage of bananas takes place following the peak of the climacteric as a result of chemical changes during the rise in temperature at the climacteric point. In other fruits, the eating ripeness stage may coincide with the climacteric.

It is also a characteristic feature of the transformations during the climacteric stage that visible fungal invasion or physiological disorders occur usually after the climacteric peak.

One feature common to most fruits exhibiting the climacteric is that they contain some reserve substance like starch or fat and that they undergo ripening after being harvested in the mature state. In contrast to such fruits, oranges, lemons and grapefruit do not undergo any ripening after they are removed from the trees

In the case of bananas, a typical course of the climacteric shows after about three or four days a generation of about fifteen c.c. of carbon dioxide per kilogram hour. This decreases in a pronounced dip until at around six or seven days it reaches a minimum point of perhaps twelve c.c. of carbon dioxide. Between the sixth or seventh

day and about the twelfth or thirteenth day, the curve rises sharply to the climacteric point, this climacteric point demonstrating a respiration of about 35 c.c. of carbon dioxide per kilogram hour. This represents a peak, the respiration declining thereafter until it reaches an approximate level of 25 c.c. of carbon dioxide around the twentieth day at which point it seems to remain fairly constant. It will be understood that this time cycle may vary somewhat depending upon temperature conditions and other influences of environment.

Other fruit such as avocados, pears, and apples demonstrate similar climacteric curves. The avocado reaches a much sharper pre-climacteric depression of respiration and a much higher and sharper rise to the climacteric maximum, whereas apples show similar but much slower curvature and pears are between apples and bananas.

Bananas are normally harvested while still green and immature, at various stages of development, e.g., the stage of development sued in connection with shipments to the United States is sometimes described as "three-quarters full" when the fruit is actually only a little more than half grown. During the fruit development, sugars remain at a very low level, while starch accumulates rapidly. The change from the unripe to the ripe stage is accompanied by a sharp rise in respiration, decrease in dry matter, hydrolysis of starch and increase in sugar content, acidity and glycoside glucose. The climacteric rise in carbon dioxide output is slightly preceded by a sharp rise in internal carbon dioxide and a marked decline in oxygen concentration. In the post-climacteric phase the decline in respiration rates is accompanied by a decrease in carbon dioxide and the partial recovery of the oxygen level. During this period, the softening tissues offer greater resistance to the movement of gases. Possibly internal anaerobic conditions bring about the production of toxic substances and are responsible for senescence and functional breakdown.

Fruit respiration is affected by temperature in the physiological range. Both excessive and insufficient temperature conditions affect the fruit. In colder environments the climacteric cycle is slowed down considerably, although there is some evidence that the total amount of carbon dioxide liberated between gathering and end of storage life is approximately the same regardless of the temperature of storage. This last fact suggests that the progressive changes in the fruit take place regardless of the temperature, but that the mechanism by which they are caused operates more slowly. These facts have a bearing upon the requirements of the present invention, since the coating used should be able to withstand cold conditions without being injured.

At higher temperatures, tests on bananas show a rapid fall in rate of respiration from a high value, a failure of the skin to develop a full yellow color, and the development of a soft and watery pulp, giving the fruit the characterization of being cooked. Temperatures below about 50° F. not only depress respiratory activity but establish in due course irreversible effects and permanent injury to the fruit. Consequently the coating must be one that does not require excessive temperatures to be applied.

It is further true that the type of atmosphere in which the fruit is stored affects the quality and durability of it. Ethylene is sometimes used, since it tends to shift the time axis for fruits that have the climacteric, normally advancing the climacteric peak in point of time. Any protective coating must not interfere with the action of ethylene, or be injured thereby.

Another interesting fact is that the emanation from plant tissue affect the maturation cycle. Tests have indicated the possibility that adjacent bananas in a more advanced state of ripeness cause the ripening of green fruit. According to Biale, ripe fruit produces active gas in sufficiently large quantities to induce an immediate rise in the rate of respiration of the preclimacteric fruit.

Likewise, gaseous products of higher plants appear to have an effect upon the maturation cycle. It has been noticed that a pronounced increase in total volatile substance occurs upon onset of fungal attack on the fruit. Other tests have indicated a sharp increase in carbon dioxide evolution by sound fruit shortly after exposure to gaseous products of the common green mold. The active emanation of the green mold accelerated also the rate of chlorophyll destruction in green fruit. Since fungus growth is undesirable, it should be suppressed.

The foregoing adequately suggests the importance of the maturation cycle in bananas and such fruits in connection with any coating applied to the fruit. Since bananas are cut from the plant when still green and must proceed through a ripening process and into the climacteric after they are harvested any protective film which is applied to cut surfaces of bananas should not interfere with overall respiration of the fruit.

It should also be possible to apply the coating to the fruit without seriously up-

setting the temperature conditions in which the fruit can be preserved. If, for example, a coating can be applied only by being heated to the temperature that causes injury to the fruit or reduces its durability, such a coating is impractical. Yet the coating should be one that will not chip off if rather cold temperatures are encountered, since sometimes it is necessary to preserve the fruit at low temperature for at least short periods of time.

Furthermore, any preservative coating applied to fruit such as bananas must not be toxic to human beings. Coatings which impart a bad taste to the fruit should be avoided for obvious reasons and preferably the coating should be digestible in case some of it is eaten. It should not, of itself, generate enamations which interfere with the maturation cycle.

In connection with bananas, the specific factors of harvesting and handling have an important effect upon preservative coatings. Bananas are harvested green. They are carried from the plantation to a processing center in the tropics, where they are washed and brought to a suitable storage temperature.

While in older days bananas attached to the main stalk were shipped as units from the Latin American countries to the United States and arrived at the retailers still attached to the main stalk, more recently bananas have been cut from the stalk and shipped in hands or clusters (partial hands) usually consisting of one to thirty bananas or fingers attached to a single crown.

Lately it has been found highly desirable to ship bananas in relatively small numbers, such as six or eight, sometimes actually separated into individual fingers, the same being boxed in Latin America or other banana growing area, and shipped to the United States or other banana consuming area where they are stored, delivered to the retailer and sold without being unboxed. Heretofore, such bananas have frequently been wrapped in some form of one of the transparent packaging films as a protective coating.

However, a problem remains even with the use of such films. A disfiguration of the fruit in the long period of storage occurs in the stem portion where it is severed from the crown. This surface darkens and shrivels due to effects of dehydration and rot and mold. This makes it unattractive in appearance and reduces the apparent quality of the bananas.

We have now developed a coating for bananas and other climacteric-exhibiting fruits which can be applied to the cut end of the bananas, be it the cut surface of the crown of a hand, the crown of a partial hand or cluster, or of an individual finger, and which prevents the unattractive decay of the cut ends. These coatings can be applied even while the fruit remains wet, and moreover, will withstand the temperature changes to which the fruit is subjected. The coatings are wax-like in appearance, edible and non-toxic, are appetizing and do not interfere with the normal ripening of the fruit.

The coatings of the present invention are composed of certain low melting point "acylated monoglycerides" (triglycerides containing at least one acyl radical and at least one fat-forming fatty acid radical).

According to the present invention, therefore, we provide a method of treating climacteric exhibiting fruits which comprises coating at least the stem portions of the fruit with a film of a glyceride having the formula:—

$$\begin{array}{l} CH_2\text{—}OR^1 \\ | \\ CH\text{—}OR^{11} \\ | \\ CH_2\text{—}OR^{111} \end{array}$$

where R^1 is an acyl radical containing from 2 to 6 carbon atoms, R^{11} is an acyl radical containing from 8 to 24 carbon atoms and R^{111} is H or an acyl radical.

The process which has been found to give best results is to melt the glyceride and dip the fruit into it. This dipping may occur soon after the fruit has been cooled to the desired storage temperature and may take place while the fruit is still moist. Bananas can be dipped until the stem ends are completely immersed, since the product does not injure the main body of the fruit or its skin. The dipping can be very brief, because all that is required is to form a continuous thin film over the stem of the fruit.

In some instances it may be desirable not to coat the body of the fruit more than necessary, but for practical reasons, it is inevitable that some of the skin below the stem will be covered when the dipping process is used. It is, however, also possible to spray the material on, to swab it on in molten form or to sponge it on. The spraying

process will be of particular applicability when the whole of the fruit is to be coated. The lower melting glycerides of the invention can be used even in the tropics because after the fruit has been cooled its temperature is maintained below 90°F.

United States Patent Specification No. 2,808,421 describes glycerides generally of the type used in the present invention and also describes one process for making them. Briefly, the process comprises transesterifying fats or oils containing fatty acid groups with lower acylated glycerides in the presence of a catalyst. A single glyceride is not formed, but rather, an equilibrium mixture of a number of different products. This equilibrium mixture can then be distilled to obtain the desired glycerides for coating the fruit.

It will be readily appreciated that the nature of the materials used in the transesterification process and the distillation conditions will naturally affect the composition of the glycerides obtained.

In order to obtain a glyceride having a suitably high melting point, the starting material should be chosen so that R^{11} contains from 14 to 20 carbon atoms. Thus, the higher acylated glyceride employed in the transesterification process should contain acyl groups having from 14 to 24 carbon atoms. However, glycerides containing R^{11} groups with from 8 to 14 carbon atoms, are also useful although they have a lower melting point.

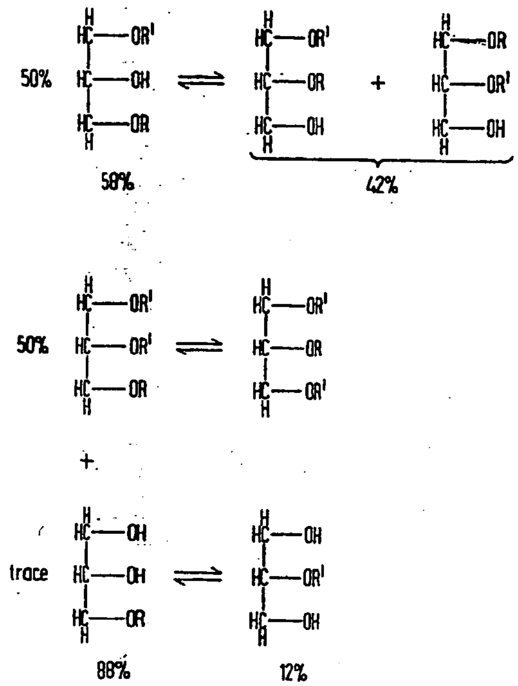
Although the glycerides containing acyl groups having from 20 to 24 carbon atoms will have suitably high melting points, they are difficult to prepare by reason of difficulties entailed in obtaining suitable starting materials for their preparation.

While the actual material used will usually be a hydrogenated lard or vegetable fat or oil, the higher acylated glycerides containing straight-chain unsubstituted fatty acid radicals will be more generally utilised. Oils such as castor oil which contain hydroxyl-substituted fatty acid radicals are not preferred for use as starting materials for the glycerides according to the invention. The higher acylated triglycerides can be either hydrogenated or unhydrogenated, the degree of hydrogenation being an important variant in determining the melting point and other physical properties of the mixed triglyceride product resulting from the present process. Examples of suitable higher acylated triglycerides are trilaurin, trimyristin, tripalmitin, tristearin and triolein; also the naturally-occurring triglycerides as are found in lard, beef tallow, cottonseed oil, soybean oil, peanut oil, coconut oil, palm oil, menhaden oil and corn oil. The term "fat-forming fatty acid radical" used herein refers to higher acyl radicals derived from naturally occurring fats and oils, whether hydrogenated or unhydrogenated.

From this it will be seen that there can be wide variation in carbon chain length for the fat and it may be saturated or unsaturated, hydrogenated or unhydrogenated.

The lower acylated glyceride used as one of the starting materials for preparing the mixed glycerides will contain from 2 to 6 carbon atoms in its acyl groups. The preferred lower acylated glyceride is triacetin although tripropionin, tributyrin, triisobutyrin, trivalerin and tricaproin may also be employed.

In the case of the mixed glyceride compositions sold under the trade name of "Myvacet 5—00" (manufactured by Distillation Products Industries, a division of Eastman Kodak Company), the following equilibrium exists between the species:—



Where R¹ is an acyl group containing 2 to 6 carbon atoms, R is long chain fatty acid acyl group greater than 6 carbon atoms. If hydrogenated animal fats have been used as the starting material in the preparation then approximately 66% of the R groups in the mixture are stearic acid acyl groups and 1/3 are palmitic acid acyl groups. In the preferred form, the acylated glyceride is prepared by acetylation of hydrogenated lard. However, it may be obtained from other than animal fats, such as vegetable fats. These interesterified molecular distilled fractions are non-fracturing, flexible, waxy solids. The preferred type used has a melting point at slightly above 37° C. and below about 160° F. and is sufficiently plastic so that it will not crack from the fruit during the storage and ripening period. It has a high oxidation stability and is soluble in alcohol. Specifically, the preferred acylated glyceride has a melting point of from 99° F. to 104° F., a viscosity of 22 cps at 122° F., an iodine value of 1 (one), and a saponification number of 320. It is approximately 7% monoglyceride. It has a peroxide value of 0.5, a stability in terms of peroxide value after ninety-six hours aeration at 98° C. of 0.5, a Reichert-Meissl value of approximately 105, and an acid value of less than 6. This type is typified by "Myvacet 7—00" of Distillation Products Industries which is obtained by acetylating approximately two-thirds of the free hydroxyl groups of hydrogenated lard monoglyceride.

Another great advantage of the preferred glyceride is that it is compatible in all proportions with fungicides so that where the fruit is treated with fungicides and thereafter treated with the acylated glyceride, there is a great suppression of fungus growth. The fungicide does not deteriorate in the presence of the acylated glyceride, but to the contrary, the expected deterioration that can occur in the absence of the acylated glyceride is reduced. While crowns treated with the acylated glyceride alone have been shown to have less susceptibility to crown rot, perhaps by providing a mechanical barrier to invasion of the fruit, some growth of mold on the crown cut surfaces treated solely with the acylated glyceride can nevertheless occur. However, when the fruit is also treated with a fungicide, the surface mold is eliminated and the crown rot is reduced to only slight amounts or almost to nothing. The fungus does not feed on the acylated glyceride. It seems, further, that the differences in effectiveness of the different basic fungicides disappear when the fungicides are combined with the glycerides according to the invention and that they become uniformly effective in controlling rot and mold. In short, with the acylated glyceride present, many otherwise less effective fungicides can be used and lower levels of fungicide concentration will be effective.

A typical test for surface mold and crown rot on bananas untreated, treated only with Myvacet 7—00, and treated also with various fungicides, is as follows:—

TABLE

SURFACE MOLD AND CROWN ROT EVALUATION OF TREATED AND UNTREATED BANANA CROWN SURFACES.

Treatment	Surface Mold ***	Crown Rot ****
Untreated (control)	5.0	2.0
"Myvacet"	1.0	1.7
Maneb	1.7	1.3
"Myvacet" & Maneb	1.0	1.3
Mixture of Sodium Salts of Dimethyl Dithiocarbamic acid and 2-mercaptobenzothiazole*	2.0	1.3
"Myvacet" & above*	1.0	1.3
Sodium Salt of Dehydroacetic acid**	2.3	1.3
"Myvacet" & above**	1.0	1.3
Zineb	3.7	1.3
"Myvacet" & Zineb	1.0	1.3
Thiram	3.3	1.3
"Myvacet" & Thiram	1.0	1.3

* Concentration — 5%

** Concentration — 1%

All others — 1:1000

*** 1 = Negative
2 = Trace
3 = Slight
4 = Moderate
5 = Severe

**** 1 = Surface discoloration only
2 = 0—1/4 of crown affected
3 = 1/4—1/2 of crown affected
4 = 1/2—3/4 of crown affected
5 = 3/4 + of crown affected

The low melting point of "Myvacet 7—00" permits it to be applied to the fruit at approximately the temperatures to which the bananas are normally subjected. It is evident from the foregoing that the approximately 100° F. melting point is within the range of temperatures that are encountered in the tropics where the fruit is grown, is cut, and initially prepared and packed.

In the above Table the names of the other fungicides are as follows: zineb is zinc ethylene bisdithiocarbamate; thiram is tetramethylthiuram disulfide. Other fungicides such as a coordination product of zinc ion and manganese ethylene bisdithiocarbamate, may be employed. In general, fungicides effective against the main types

of organisms responsible for rot and mold, namely, Thielaviposis, Glocosporium and Fusarium may be utilized.

The fungicide usually is used in weight ratio of 1 to 1000 with respect to the glyceride. It is usually added as a solid to the melted glyceride and physically mixed therewith to make a uniform suspension. Higher concentrations with respect to the glyceride of 5% in the case of the mixture of sodium salts of dimethyl dithiocarbamic acid and 2-mercaptobenzothiazole and 1% in the case of the sodium salt of dehydroacetic acid are used to advantage.

Bananas having their stems coated with the acylated glyceride aforesaid, especially those also having fungicide or fungistatic material thereon, have been shown to have very little decay of the stems after eight or nine days' storage, even though the uncoated parts of the skins had become quite dark. The fruit remains unspoiled. The stem of the control fruit used for comparison had become dark and shrivelled.

The significance of this invention may be realized by considering that fruit grown in more distant countries can be successfully packaged in such countries and shipped to the United States or Europe or Asia. Heretofore the decay of the stems during the extended shipping period could be so bad that the fruit could only be sold as inferior grade or with extensive loss in quality. By preventing this decay and enabling the fruit to be displayed for sale with no apparent decay, new markets for the bananas grown in distant countries are opened up.

WHAT WE CLAIM IS:—

1. A method of treating climacteric exhibiting fruits which comprises coating at least the stem portions of the fruit with a film of a glyceride having the formula:—

$$\begin{array}{l} CH_2\text{—}OR^1 \\ | \\ CH\text{—}OR^{11} \\ | \\ CH_2\text{—}OR^{111} \end{array}$$

where R^1 is an acyl radical containing from 2 to 6 carbon atoms, R^{11} is an acyl radical containing from 8 to 24 carbon atoms and R^{111} is H or an acyl radical.

2. A method according to claim 1 in which only the cut stem portions of the fruit are coated with the glyceride.

3. A method according to claim 1 or 2 in which R^{11} is an acyl radical containing from 14 to 20 carbon atoms.

4. A method according to any of claims 1 to 3 in which the coating is applied by dipping the desired portions of the fruit into a molten bath of the glyceride.

5. A method according to any of claims 1 to 4 in which the glyceride has a melting point of from 99° to 104° F., a viscosity of 22 cps at 122° F., an iodine value of 1 and a saponification number of 320.

6. A method according to any of claims 1 to 5 in which the fruit is previously coated with a fungicide or fungistatic agent.

7. A method according to any of claims 1 to 5 in which a fungicide or fungistatic agent is mixed with the glyceride before the glyceride is applied to the fruit.

8. A method according to claim 7 in which the weight ratio of the fungicide or fungistatic agent is 1:1000.

9. A method according to any of claims 6 to 8 in which the fungicide is manganese ethylene bisdithiocarbamate, a mixture of the sodium salts of dimethyl dithiocarbamic acid and 2-mercaptobenzothiazole, the sodium salt of dehydroacetic acid, zinc ethylene bisdithiocarbamate, tetramethylthiuram disulfide or the coordination product of the zinc ion and manganese ethylene bisdithiocarbamate.

10. A method according to claim 7 in which the fungicide is a mixture of the sodium salts of dimethyl dithiocarbamic acid and 2-mercaptobenzothiazole and fungicide is used in the proportion of 5% by weight of the glyceride.

11. A method according to claim 7 in which the fungicide is the sodium salt of dehydroacetic acid and is used in the proportion of 1% by weight of the glyceride.

12. A process of treating climacteric exhibiting fruits substantially as herein described.

13. Climacteric exhibiting fruits when treated by a process claimed in any of the preceding claims.

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